Dyes and Pigments 133 (2016) 467–478

Contents lists available at ScienceDirect

Dyes and Pigments

journal homepage: www.elsevier.com/locate/dyepig

Development of self-curable hybrid pigment inks by miniemulsion polymerization for inkjet printing of cotton fabrics

Mahmoud Elgammal [a, *], Reinhold Schneider [b], Michael Gradzielski [a]

[a] Stranski-Laboratorium Fuer Physikalische and Theoretische Chemie, Institut Fuer Chemie, Strasse des 17, Juni 124, Sekr. TC7, Technische Universitaet Berlin, D-10623, Berlin, Germany
[b] Institut Fuer Textilchemie und Chemiefasern (ITCF), Koerschtalstrasse 26, 73770, Denkendorf, Germany

ARTICLE INFO

Article history:
Received 6 January 2016
Received in revised form
19 April 2016
Accepted 21 June 2016
Available online 22 June 2016

Keywords:
Pigment encapsulation
Inkjet printing
Miniemulsion polymerization
Copolymer
Colloidal stability

ABSTRACT

In our work, organic pigments were encapsulated with a polymer latex layer to reduce the tendency for pigment agglomeration and improve their stability in aqueous ink dispersions. Such polymer-encapsulated pigments then were applied in inkjet printing without addition of separate binder additives, thereby reducing the risk of unfavorable interactions between the separate latex and pigment particles. We studied systematically the encapsulation of C.I. Pigment red 112 by miniemulsion polymerization of pigment/butyl acrylate-*co*-methyl methacrylate (BA-MMA) or styrene-co-butyl acrylate (St-BA) copolymers. The ratio of monomer to pigment was varied to find optimum conditions for the preparation of self-curable hybrid pigment inks for the textile inkjet printing application. Inkjet printing of cotton fabrics with different encapsulated and non-encapsulated pigment colors shows that the encapsulated pigment/polymer latex particles yield equally good values in terms of color strength, rubbing and washing fastness in comparison to non-encapsulated conventional inks, but avoiding problems of clogging and colloidal instability.

1. Introduction

Inkjet printing is considered one of the most promising methods for the printing of textile fabrics and therefore has received intense attention from both academic and industrial research. This evolving technology offers significant advantages over conventional textile printing methods such as, the simple and fast procedures, the options for small scale and customized production, low pollution, low cost by reduction of water and energy consumption [1–5]. Inks for fabric printing are usually classified into two categories, dye-based and pigment-based inks. The pigment-based inks type has become more popular because of its ability to give fuller and brighter shades without the need for any pretreatments as well as the better washing and light fastness and the applicability to all types of textile fabric substrates [6]. The pigment and binder are the principle ingredients in the pigment-based ink formulations of the textile inkjet printing. Pigments are typically manufactured with particle sizes below 500 nm in order to deliver optimum color conditions and other appearance properties such as opacity and gloss [7]. However, the pigment particles tend to agglomerate in aqueous and non-aqueous dispersions due to their high surface area and the pronounced attractive van der Waals forces between the particles. This in turn can lead to serious problems during jetting of inks such as clogging the nozzles of the inkjet printer. In addition, the agglomeration reduces the pigment efficiency and the smoothness of the printed fabrics by the appearance of aggregates on the film surface, resulting finally in a lower product quality.

Therefore, it is crucial to develop pigment ink dispersions methods to prevent the association and agglomeration of the pigment particles. Furthermore, by controlling the particle size one can enhance the stability of the pigment ink dispersions. In this regard, the encapsulation of the pigment particles with a polymer layer is an alternative way to minimize the risk of particle agglomeration and thereby improving the dispersibility and stability of pigment inks. Moreover, pigment encapsulation protects the pigment particles from the effect of the UV radiation or the pH variation. Recently, several methods have been reported for the encapsulation of pigment particles such as dispersion, emulsion and miniemulsion polymerization [8]. Conventional emulsion polymerization was used to encapsulate inorganic particles such as

* Corresponding author.
E-mail addresses: elgammally@yahoo.com (M. Elgammal), michael.gradzielski@tu-berlin.de (M. Gradzielski).

http://dx.doi.org/10.1016/j.dyepig.2016.06.033
0143-7208/

colloidal silica [9], titanium dioxide pigments [10], silver particles [11], and organic pigments [12]. However, emulsion polymerization generated insufficient encapsulation efficiencies, due to the complexity of the nucleation mechanism in this process. In the last 10 years, some work has described the encapsulation of organic and inorganic pigments by miniemulsion polymerization [13–15]. Miniemulsion polymerization differs from conventional emulsion polymerization in the mechanism of the particle nucleation, which takes place in the stabilized monomer droplets [16,17]. Accordingly, the introduction of the pigment particles to the stabilized droplets by miniemulsification leads to high encapsulation efficiencies upon subsequent polymerization.

In this work, we aimed at preparing water based hybrid dispersions of polymer encapsulated organic pigment inks in order to enhance the stability and dispersibility of the ink formulations by reducing the pigment particle–particle interactions and thereby lowering the risk of the agglomeration of the pigment particles. In addition, the encapsulated pigments were applied successfully as inks for cotton fabrics without adding separate polymer or copolymer binders to the inkjet printing formulations, which allows the hybrid ink to have dual property, creating a polymer film during curing on the substrate and fulfilling the basic role of inks as color delivery.

We have achieved the encapsulation with different pigment colors but focused our detailed study on the C.I. Pigment Red 112, an azo-naphthalene based pigment color stuff widely used for textile coloration. The encapsulation was performed by the miniemulsion polymerization method using the co-sonication technique with butyl acrylate-*co*-methyl methacrylate (BA-co-MMA) or styrene-co-butyl acrylate (St-co-BA) copolymer latexes. The anionic surfactant SDS was used to stabilize the pigment dispersions and miniemulsions and hexadecane was employed as co-stabilizer for the miniemulsion preparations. The pigment-polymer weight ratio has been varied in order to study its influence on the encapsulation efficiencies as well as the physical properties and the printing behavior of the ink formulations and finally to achieve an optimum hybrid ink recipe. The particle size, morphology, encapsulation efficiency, thermal analysis, stability, rheology and other physical properties of the encapsulated pigments were studied. Of course, a key aspect here is confirming and quantifying the encapsulation efficiency, which is not an obvious task. Finally, the properties of the printed cotton fabrics with the encapsulated hybrid-pigments were compared to conventional inks.

The general aim of this investigation was to optimize by a miniemulsion-based polymerization in a systematic way the conditions for preparing latex encapsulated pigments with long-time stability and low tendency of clogging of printing nozzles, which are essential prerequisites for their successful application in ink jet printing.

2. Experimental section

2.1. Materials

Butyl acrylate (BA), methyl methacrylate (MMA) (BASF), and styrene (Sigma-Aldrich) monomers were purified by distillation under reduced pressure before use. Azobisisobutyronitrile (AIBN) (Sigma Aldrich) sodium dodecyl sulfate (SDS, Fisher), hexadecane (HD, Sigma-Aldrich, 99%), and sodium bicarbonate (BDH, 99%) were used as received. Millipore water was used in all waterborne polymerizations. The pigments stuffs C.I. Pigment red 112(PR112), C.I. Pigment blue (PB. 15:3) and C.I. Pigment yellow PY.155 were obtained from Clariant. The chemical structure of the different organic pigments is described in Fig. S1. BYK®-346 was supplied from BYK Chemie GmbH. Cotton fabric (100% bleached, plain weaved, 140 g/m^2) was used as substrate for the inkjet printing.

2.2. Pigment dispersion and encapsulation

2.2.1. Dispersion of the pigment colors in aqueous medium

The aqueous dispersion of pigments were prepared by dispersing 10 g of the pigment color with 1.75 g SDS in 88.25 g Millipore water. The pH of the dispersions was adjusted to 8 by adding sodium hydroxide (0.1 M NaOH). The pigment dispersions were stirred overnight and then sonicated by the ultrasonic processor (Branson digital model 250) for 120 min at 70% amplitude. To reduce any rise in temperature that may occur during the pigment dispersion, the sonification processes were done with 5 s pulse on and 10 s pulse off cycles under ice-cooling.

2.2.2. Encapsulation of the pigment colors with the BA-MMA and St-BA copolymer latexes

The miniemulsion recipe listed in Table 1 was prepared in order to add it later to the different pigment dispersions with different monomer/pigment weight ratios. The miniemulsification started by mixing the different monomers, hexadecane and the oil soluble AIBN initiator for 15 min by magnetic stirring. Then the mixture was added to a solution of sodium dodecyl sulfate (SDS) and sodium bicarbonate and stirred for 20 min. Finally, the miniemulsion was prepared by sonification of the mixture by the ultrasonic processor (Branson digital model 250) for 10 min, at 70% amplitude with 5 s pulse on and 10 s pulse off cycles under ice cooling. It should be noted that the BA-MMA and St-BA miniemulsion comonomers were prepared in different monomer ratios. The encapsulation started by adding the proper amount of the miniemulsion which corresponded to the different monomer/pigment mass ratios 0.11, 0.25, 0.42, and 0.66–40 g of each pigment dispersion. The monomer miniemulsion/pigment dispersion was stirred for 30 min then pulse sonicated for 5 min at 70% amplitude. This process was repeated twice and the all the sonication processes were carried out under ice cooling. Finally, the polymerization was carried out at 70 °C overnight [18].

2.3. Characterization and analytical methods

2.3.1. Particle size and polydispersity analysis

Particle size, size distributions and morphology were determined using different techniques such as dynamic light scattering (DLS), disc centrifuge (DC) and transmission electron microscopy (TEM).

Dynamic Light Scattering (DLS) measurements were performed at 25 °C with a setup consisting of an ALV 7004 correlator, an ALV CGS-3 goniometer and a He–Ne laser with a wavelength of 632.8 nm. Cylindrical glass sample cells of 0.8 cm diameter were placed in an index-matching vat filled with toluene. The ink dispersion was diluted by ~100 times with distilled water prior to the measurements and the intensity autocorrelation functions were recorded at an angle of 90°. The obtained autocorrelation functions were then analyzed by the CONTIN method in order to

Table 1
Miniemulsion recipe.

Ingredients	Weight (g)
DI Water	80
Monomers, BA, St, MMA	20
SDS	1.38
HD	0.72
Buffer($NaHCO_3$)	0.0067
AIBN	0.83